X-ray Absorption Spectroscopic Investigation of Arsenite and Arsenate Adsorption at the Aluminum Oxide–Water Interface

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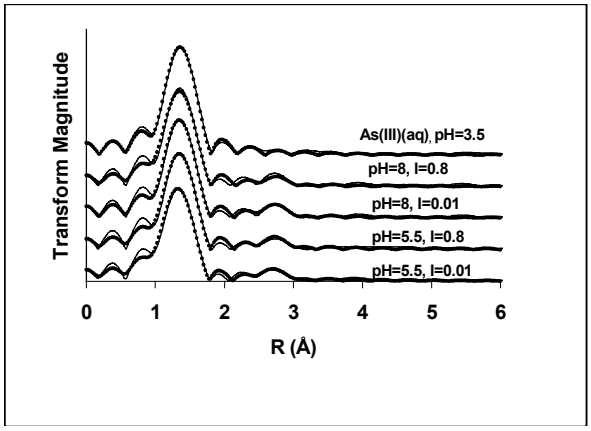
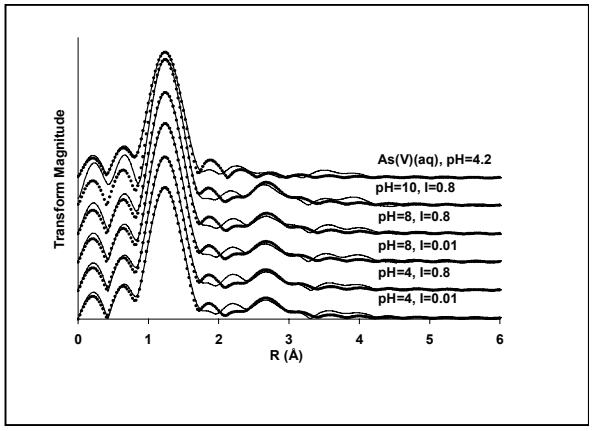
Introduction: We investigated the As(III) and As(V) adsorption complexes forming at the γ-Al_2O_3 / water interface as a function of pH and ionic strength (I), using a combination of adsorption envelopes, electrophoretic mobility(EM) measurements and X-ray absorption spectroscopy (XAS). The As adsorption envelopes show that 1) As(III) adsorption increases with increasing pH and is insensitive to I changes (0.01 M and 0.8 M $NaNO_3$) at pH=3-4.5, while adsorption decreases with increasing I between pH = 4.5 and 9.0, and 2) As(V) adsorption decreases with increasing pH and is insensitive to I changes at pH=3.5-10. The EM measurements show that As(III) adsorption does not significantly change the EM values of γ-Al_2O_3 suspension in 0.1M $NaNO_3$ at pH = 4-8, whereas As(V) adsorption lowered the EM values at pH = 4-10. The EXAFS data indicate that both As(III) and As(V) form inner-sphere complexes with a bidentate binuclear configuration, as evidenced by a As(III)-Al bond distance of $\cong$3.22 Å and a As(V)-Al bond distance of $\cong$ 3.11 Å. The As(III) XANES spectra, however, show that outer-sphere complexes are formed in addition to inner-sphere complexes, and that the importance of outer-sphere As(III) complexes increases with increasing pH (5.5 to 8) and with decreasing I. In short, the data indicate for As(III) that inner- and outer sphere adsorption co-exist whereas for As(V) inner-sphere complexes are predominant under our experimental conditions.





Fourier transforms (RSF) of the χ-functions of As(III and V))/γ-Al_2O_3 adsorption samples. The solid lines are the experimental data and the dotted lines represent the theoretical multishell fit to the data.